FINAL REPORT TO THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

ON

STUDIES RELATING TO THE SYNTHESIS OF MONOMETHYLHYDRAZINE

BY CHLORAMINATION

AFOSR-80-0007

AND

PROBLEM RELATING TO THE PROTECTION OF THE ENVIRONMENT

FROM THE VAPORS OF 1,1-DIMETHYLHYDRAZINE,

MONOMETHYLHYDRAZINE AND HYDRAZINE

For Period of October 1, 1979 to June 30, 1981

Principal Investigator

Harry H. Sisler

Co-Investigator

Milap A. Mathur

Department of Chemistry

University of Florida

Gainesville, Florida 32611

September 30, 1981

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 81-0769	2. GOVT ACCESSION NO. AD A108367	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Studies Relating to the Synthesis of Monomethylhydrazine by Chloramination and Problem Relating to the Environment from the Vapors of 1,1-Dimethylhydrazine and Hydrazine		5. TYPE OF REPORT & PERIOD COVERED Final 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Harry H. Sisler		8. CONTRACT OR GRANT NUMBER(s) AFOSR-80-0007
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Florida Department of Chemistry Gainesville, Florida 32611		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/B2
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NC Bldg. 410, Bolling AFB, DC 20332		12. REPORT DATE 30 September 1981 13. NUMBER OF PAGES 7
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Monomethylhydrazine	1,1-Dimethylhydrazine
Hydroxylamine-O-Sulfonic Acid	Dimethylhydrazine
Methylamine	Formaldehyde Dimethylhydrazone

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The synthesis of monomethylhydrazine was successfully achieved by reacting solutions of hydroxylamine-O-sulfonic acid with methylamine in diglyme. The synthesis of 1,1-dimethylhydrazine was carried out in a similar manner with dimethylhydrazine. A mechanism for the formation of formaldehyde dimethylhydrazone by the reaction of dimethylamine and chloramine was proposed. A study was conducted on the oxidation of monomethylhydrazine and 1,1-dimethylhydrazine by oxygen.

DD FORM 1 JAN 73 1473

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

INTRODUCTION

This progress report summarizes the results obtained on the project entitled "Studies Relating to the Synthesis of Monomethylhydrazine by Chloramination and Problems Relating to the Protection of the Environment from the Vapors of 1,1-Dimethylhydrazine, Monomethylhydrazine and Hydrazine", a proposal approved by the Air Force Office of Scientific Research in 1979. The starting date of the proposed research was October 1, 1979. This project was, in fact, the continuation of the on-going project entitled "Basic Studies Relating to the Synthesis of Unsymmetrical Dimethylhydrazine, and Monomethylhydrazine by Chloramination". A final report relating to the results obtained on the original project from the period September 1, 1975 to September 30, 1979 at the University of Florida was submitted to the Air Force Office of Scientific Research on December 7, 1979. Since these two projects were interrelated, some remaining work of the original project was also completed between the period of October 1, 1979 and June 30, 1981. These results are included in this report.

1. Syntheses of Monomethylhydrazine.

(a) By the Reaction of Methylamine and Hydroxylamine-O-Sulfonic Acid.

The synthesis of monomethylhydrazine was successfully achieved by reacting solutions of NH_2OSO_3H with CH_3NH_2 in diglyme. For example, 0.37 mol of NH_2OSO_3H was mixed with 1.7 mol of CH_3NH_2 in dry diglyme at -10°C. The total yield of N-N bonded material, based on NH_2OSO_3H taken, was 55%. On fractional distillation of the reaction mixture

on a spinning bond column a mixture containing 84.3% monomethylhydrazine, 11.5% methanol and a small amount of methylamine, water and solvent was obtained. The products of this mixture were identified by gas chromatographic analysis as well as by ^1H nuclear magnetic resonance spectroscopy. The complete results of this study were reported in Inorg. Chem., 1980, 19, 2846. A reprint is included in Appendix I.

(b) By the Chloramination of Methylamine by Chloramine.

The study relating to the synthesis of monomethylhydrazine by the chloramination of methylamine begun earlier was completed during this project period. The reaction between CH_3NH_2 and NH_2Cl was studied under the following conditions: (1) In presence of KOH and NH_3, (2) in presence of CH_3ONa and NH_3, and (3) in absence of NH_3 and fixed base. Monomethylhydrazine formation was observed in (1) and (2) and a yield of total hydrazine content up to 84% was observed. It is therefore evident that a permanent base like KOH or CH_3ONa is favorable for formation of monomethylhydrazine in the chloramination of methylamine. The details of this study are reported in the Inorg. Chem., 1980, 19, 2192. A reprint is included in Appendix II.

2. Syntheses of Unsymmetrical Dimethylhydrazine.

(a) By the Reaction of Dimethylamine with Hydroxylamine-O-Sulfonic Acid.

The synthesis of 1,1-dimethylhydrazine was successfully carried out by the treating solutions of NH_2OSO_3H with $(CH_3)_2NH$ in diglyme.

For example, 0.15 mol of NH_2OSO_3H was mixed with 1.78 mol of $(CH_3)NH$ in diglyme at -78°C. After the reactants were mixed the reaction mixture was brought to 25°C. The reaction mixture was filtered to remove $[(CH_3)_2NH_2]_2SO_4$ and was then distilled over KOH. The fraction distilling between 60-64°C was collected. The gas chromatographic analysis of this distillate showed 81.5% of 1,1-dimethylhydrazine. The other products were dimethylamine 9.1%, 1,1,4,4-tetramethyl-2-tetrazene 1.44%, and diglyme 1.63%. No formaldehyde dimethylhydrazone was detected. The complete results of this study are reported in Inorg. Chem., 1980, 19, 2846. (Appendix I).

(b) By the Reaction of a Chloramine-Ammonia Mixture with Dimethylamine in the Presence of KOH.

For example, a solution containing 0.5 mol of $(CH_3)_2NH$ and 0.2 mol of KOH in n-butanol was treated with the NH_2Cl-NH_3effluent (.1 mol NH_2Cl) of the chloramine generator at -78°C. The volatile gases were allowed to escape. The solid formed was removed by filtration and the solution was fractionally distilled. The 1,1-dimethylhydrazine obtained was estimated by ^1H NMR analysis. The yield of the 1,1-dimethylhydrazine based on NH_2Cl used was 30%. The details of this study are reported in Ind. and Eng. Chem. Prod. Res. Dev., 1981, 20 181-5 (Appendix III).

3. Studies of the Mechanism of the Formation of Formaldehyde Dimethylhydrazone.

The study of the formation of formaldehyde dimethylhydrazone was

completed and a mechanism for the formation of formaldehyde dimethylhydrazone by the reaction of dimethylamine and chloramine was proposed. The results of this study have been published in Ind. and Eng. Chem. Prod. Res. Dev., 1981, 20, 181-5. It is worthwhile to note that the reaction between $(CH_3)_2NNH_2$ and NH_2Cl is very fast and, therefore, that NH_2Cl could be used to remove $(CH_3)_2NNH_2$ vapors from the atmosphere using a NH_2Cl solution in the scrubbers. A reprint is included in Appensix III.

4. Studies Relating to the Oxidation of 1,1-Dimethylhydrazine by Oxygen.

The original paper on the "Oxidation of 1,1-Dimethylhydrazine by Oxygen" was submitted in early 1979. A revised version of this study was prepared in compliance with the referee's comments and has been published in Inorg. Chem., 1981, 20, 426-429. A reprint is included in Appendix IV. This study was conducted to examine the problems relating to the protection of the environment from the vapors of 1,1-dimethylhydrazine and its oxidation products.

5. Oxidation of Monomethylhydrazine.

The interaction of monomethylhydrazine with oxygen was investigated. The results may be summarized as follows:

(a) Reaction of Monomethylhydrazine with Oxygen without Solvent.

This study was conducted before the current project period and the results are summarized in the "Final Report to the Air Force Office of the Scientific Research on the 'Basic Studies Relating to the

Synthesis of Unsymmetrical Dimethylhydrazine and Monomethylhydrazine by Chloramination'" submitted on December 7, 1979.

(b) Oxidation of Monomethylhydrazine by Oxygen in Ether Solution at 25°C.

For example, monomethylhydrazine (2.3 g, .050 mol) and 1 g benzene were dissolved in 100 mL of ether solution, and were transferred into a 2.45-liter reaction vessel containing pure oxygen at 25°C and 761 mm of Hg pressure. The zero time of the reaction was recorded. The zero reading of the methylhydrazine concentration was determined by comparing the chromatographic peak areas of methylhydrazine and benzene before mixing with oxygen. The progress of the reaction was followed by observing the ratio of the areas of the gas chromatographic peaks of CH_3NHNH_2 and C_6H_6 as a function of time. Typical results are summarized in the following table:

Time in minutes	$\frac{CH_3NHNH_2 \text{ peak area}}{C_6H_6 \text{ peak area}}$
0	0.16
9	0.16
17	0.11
26	0.0
40	0.0

The other products detected by gas chromatographic analysis were formaldehyde monomethylhydrazone or its dimer, methanol, and water. In conclusion, monomethylhydrazine is quickly oxidized by the oxygen and, therefore, quickly removed from the atmosphere.

A spinoff from this research was the discovery that the oxidation of methylhydrazine by mercuric oxide yields appreciable amounts of the highly toxic mercury dimethyl. This was reported in the J. Org. Chem., 45, 1329 (1980). A reprint is included in Appendix V.

6. Synthesis of Unsymmetrical Di-isopropyl Hydrazine by the Chloramination of Di-isopropylamine.

The chloramination of di-isopropylamine was carried out in ethylether and also in diglyme. No hydrazine was obtained in either instance. The chloramination reaction was also carried using the pure amine without dilution. In this case $(i\text{-}C_3H_7)_2NNH_2$ was obtained in 75% yields. No evidence of the formation of $(CH_3)_2NN{=}C(CH_3)_2$ was obtained. This supports our previously reported mechanism for the formation of $(CH_3)_2NN{=}CH_2$ in the chloramination of dimethylamine since $[(CH_3)_2CH]_2\overset{+}{N}{=}\ddot{\overset{-}{N}}:$ would be less likely to undergo the nucleophilic reaction analogous to that postulated for $(CH_3)_2\overset{+}{N}{=}\ddot{\overset{-}{N}}:$ (Appendix III). These results have been accepted for publication in the J. Inorg. Nucl. Chem. (Appendix VI).